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High resolution studies of low-energy electron attachment to SF_5Cl: Product anions and absolute cross sections

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Abstract

Low-energy electron attachment to SF_5Cl was studied at high energy resolution by mass spectrometric detection of the product anions. Two variants of the laser photoelectron attachment (LPA) technique (Kaiserslautern) were used for determining the threshold behaviour of the yield for SF_5^- formation at about 1 meV resolution, and to investigate the relative cross sections for Cl^-, FCl^-, and SF_5^- formation towards higher energies (up to 1 eV) at about 20 meV resolution. Thermal swarm measurements (Birmingham) were used to place the relative LPA cross sections on an absolute scale. A trochoidal electron monochromator (Innsbruck) was used for survey measurements of the relative cross sections for the different product anions over the energy range of 0–14 eV with a resolution of 0.30 eV. Combined with earlier beam data (taken at Berlin) [M. Fenzlaff, R. Gerhard, E. Illenberger, J. Chem. Phys. 88 (1988) 149], the present experimental results provide a detailed set of partial cross sections for anion formation in low-energy electron collisions with SF_5Cl.
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1. Introduction

Electron attachment investigations of sulfurhexafluoride (SF_6) and its derivates (such as SF_5Cl) provide insights into the physical and chemical molecular properties of electron capture processes, and hence are of general interest. This is particularly true when one considers the importance of SF_6 in plasma-etching applications in industry [1,2] and as an insulating dielectric [3,4]. Electron attachment data need to be incorporated into models used to characterize gaseous discharges and industrial plasmas. Thus, a thorough understanding of this fundamental and significant collision process may lead to an enhancement of the potential applications of technological plasmas. For SF_6 the dominant process at very low electron energies is the formation of the long-lived parent anion SF_6^-. It is thus of special interest to examine to what extent long-lived SF_5Cl^- anions are formed in electron capture by SF_5Cl at near-zero energies.

To date, only few studies have investigated electron attachment to SF_5Cl [5–8]. In a pioneering work, Harland and Thynne [5] studied electron-impact induced positive and negative ion formation by means of time-of-flight mass spectrometry. For the anions they reported relative intensities measured at two electron energies, 2 and 70 eV. In both cases the dominant anion was F^- (=100), followed by Cl^- (2.7 or 10) and SF_5^- (2 or 2.4), the relative intensities at 2 and 70 eV, respectively, being given in brackets. At energies below 1 eV, they only observed SF_5^- with the maximum yield located at 0.7 eV. The anion yield for F^- showed two major peaks located at 5.1 and 9.4 eV and a rise towards another peak below 2 eV. The energy resolution of this work was rather low (the peak half width for SF_6^- from SF_6 amounted to 0.6 eV) and the quoted peak energies appear to be too high by about 0.6 eV. In a later mass spectrometric study of SF_5Cl, carried out with an energy-selected electron beam of about 0.25 eV width, Fenzlaff et al. [6] measured relative cross sections for nine anions over the energy range 0–19 eV.

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They found as dominant anions (intensities at the respective low-energy maximum in brackets) F^- (40), Cl^- (60), FCl^- (20), and SF_5^- (10), and a small amount of the parent anion SF_5Cl^- (0.5) for which the detection time was about 40 μs. At higher energies the fragments F_2^-, SF_2^-, SF_3^-, and SF_4^- were also observed. The yield for SF_5Cl^-, Cl^-, and FCl^- peaked at near-zero energy while that for SF_5^- showed a maximum at about 0.3 eV. The cross section for F^- formation exhibited three maxima located at about 0.7, 4.5 and 8.8 eV; the latter two correspond to the two higher energy peaks reported by Harland and Thynne [5].

Subsequently, an electron swarm measurement [7] revealed that the major products resulting from electron attachment using a cloud of electrons with a thermal (Maxwellian–Boltzmann) electron energy distribution at 300 K in CO_2 carrier gas (typically at 1 bar) are $SF_5Cl^- \approx 10\%$ and $SF_5^- \approx 90\%$. The high fraction of the parent anion SF_5Cl^- can be attributed to collisional stabilization of the initially formed SF_5Cl^- complex while the observation of SF_5^- as the dominant anion agrees with the findings of Harland and Thynne [5], but is in notable contrast to the observations of Fenzlaff et al. [6]. An earlier non-thermal swarm measurement, whilst agreeing with the thermal measurements at low electron mean energies, indicated that SF_4^- became the dominant anion as the mean electron energy of the swarm increased above 0.2 eV [8].

The question then is how to reconcile the different observations. With the aim to clarify the situation and to provide highly resolved absolute attachment cross sections, two new independent electron beam studies of SF_5Cl were carried out at Innsbruck and Kaiserslautern. The investigation at Innsbruck used a trochoidal electron monochromator (energy resolution about 0.3 eV) and a quadrupole mass spectrometer [9] to measure partial anion yields over the energy range 0–14 eV. The work at Kaiserslautern used the laser photoelectron attachment (LPA) method [10] which allows attachment cross sections to be measured at energy resolutions down to about 1 meV, and the recently introduced extended laser photoelectron attachment (EXLPA) technique (resolution around 20 meV, energy range 0–1 eV) [11]. Taken together, these experiments provide a set of complementary relative cross sections. Furthermore, using the thermal value of the attachment rate coefficient for SF_5Cl measured by Mayhew et al. [7], the relative (EX)LPA cross sections were converted into absolute values.

The paper is organized as follows: in Section 2 we describe the experimental setups and some test measurements. In Section 3 we present experimental results and compare them with previous work. From the highly resolved absolute cross section for anion formation at low energies, we can also calculate thermal attachment rate coefficients as a function of electron temperature (100–10,000 K) for a fixed gas temperature 300 K.

2. Experimental

2.1. Laser photoelectron attachment (LPA/EXLPA; Kaiserslautern)

High resolution measurements of anion formation resulting from electron attachment to SF_5Cl over the energy range 0.001–1 eV were obtained using two variants of the LPA method [10,11]. In summary, a static target gas at a temperature of $T_G = 300$ K was used in conjunction with a pulsed electron production and anion extraction scheme, followed by mass spectrometric anion detection. Photoelectrons are created from an atomic beam by resonant two-step photoionization of potassium atoms in their ground state, and currents of typically 35 pA were used.

In the standard LPA experiment, the atomic beam is crossed by two collinear laser beams in the center of the reaction chamber, and the photoelectrons produced interact with the target molecule in the region where the photoionization process takes place. The anions formed are extracted by a pulsed electric field (repetition rate 100 kHz), during which the production of photoelectrons is interrupted. The anions are then imaged into a quadrupole mass spectrometer, and the mass-selected ions are detected by a differentially pumped off-axis channel electron multiplier. The electron energy resolution achieved depends on several experimental factors such as the bandwidth of the lasers, residual ac and dc electric fields, the electric field due to the presence of the K^+ ions produced by photoionization of the potassium beam (i.e., the space charge effect) and the Doppler effect. For the LPA data, this resolution amounts to 1–2 meV over the energy range 1–200 meV, the energy range being limited by the tuning range of the photoionization laser.

Higher electron energies were accessed by the EXLPA method [11]. In this experiment, near-zero energy photoelectrons are produced in a separate ionization chamber, are accelerated by a weak electric field in a guiding magnetic field, brought to the energy of interest prior to traversal through the target region, and are subsequently accelerated and deflected onto a collector plate. The energy resolution in the EXLPA experiments amounted to about 20 meV.

The LPA and EXLPA anion yields were found to be in good agreement over the range 50–200 meV. Absolute attachment cross sections $\sigma_A(E) = NY_A(E)$ were established by normalization of the measured anion yield $Y_A(E)$ (i.e., the relative dissociative electron attachment cross section) to the recommended thermal energy attachment rate coefficient $k_A(T = T_e = T_G = 300\,\mathrm{K}) = 2.0 \pm 0.3 \times 10^{-8}\,\mathrm{cm^3\,molecule^{-1}\,s^{-1}}$ [7,8] using the expression (see, e.g., [10]):

$$k_A(T_e; T_G) = N(2/m_e)^{1/2} \int_0^\infty Y_A(E; T_G) E^{1/2} f(E; T_e)\,dE \quad (1)$$

N is the normalization constant, m_e is the electron mass; the electron energy distribution function $f(E;T_e)$ is assumed to be Maxwellian and given by $f(E;T_e) = (4/\pi)^{1/2}(k_B T_e)^{-3/2} E^{1/2} \exp(-E/k_B T_e)$ where $k_B T_e = 25.85$ meV for $T_e = 300$ K and $\int_0^\infty f(E; T_e)\,dE = 1$. Note that the attachment yield $Y_A(E;T_G)$ in general depends on the gas temperature T_G.

In addition to these free electron attachment studies with the LPA/EXLPA methods, we also investigated Rydberg electron transfer (RET) to SF_5Cl. The RET method investigates the production of state-selected Rydberg atoms (in the present experiment $K^{**}(n\mathrm{s}, n\mathrm{d})$) and their reaction with SF_5Cl. At high

principal quantum numbers ($n \geq 30$) the mean distance between the Rydberg electron and the atomic nucleus is so large that the influence of the latter on the collision process via post-attachment interactions [12] can be neglected. The Rydberg electrons can then be interpreted as essentially free and react with the target with an electron velocity distribution $f_{nl}(v)$ characteristic of the nl Rydberg state [12,13].

2.2. Electron beam apparatus (Innsbruck)

The electron attachment spectrometer in Innsbruck consists of a molecular beam system, a trochoidal electron monochromator (TEM) and a quadrupole mass filter with a pulse counting system for detecting product ionic species [9]. For the set of experiments presented here the TEM was operated with an energy resolution of 0.30 eV as a compromise between product ion intensity and incident electron energy resolution. SF_5Cl was expanded at a pressure of about 10 mbar through a 20 μm nozzle into the attachment region, and the whole apparatus was kept at a constant temperature before and during the measurements of about 328 K. The electron beam intersected the effusive beam of SF_5Cl at right angles. The product anions were subsequently drawn out of the collision region by a small electrostatic field and focussed onto the entrance of a quadrupole mass spectrometer. The mass-selected anions were detected by a channel electron multiplier. Details on SF_5Cl pressure and electron current were recorded throughout the measurements to allow for normalization. The energy scale was calibrated by recording SF_6^- from SF_6. This was chosen rather than using Cl^- from CCl_4, because of the problem of removing residues of CCl_4 from the instrument in comparison to pumping away any remaining SF_6. Given that one of the major discrepancies between the results of Fenzlaff et al. [6] and the Birmingham swarm measurements is the observation that in the former study Cl^- is the dominant product species, we wished to remove any possibility of contamination which could lead to Cl^- being produced.

2.3. Electron swarm mass spectrometer (Birmingham)

As mentioned above, the initial swarm study [8] yielded differences with regard to the results of the earlier beam measurements [5,6]. Whilst this paper is focused on the recent LPA and electron beam investigations, some of the data from the swarm investigations will be reported here for completeness. Details of an upgraded swarm apparatus, which was used to check the earlier swarm data, have recently been published [7].

2.4. Molecular sample

Samples of SF_5Cl were commercially purchased (Apollo Scientific Limited) with a stated purity of 97%, and were used without further purification. We were unable to obtain any information on the possible impurities within our sample from the supplier. However, as part of our general study at Innsbruck of the molecular properties of SF_5Cl we investigated its positive ion spectra, and recorded appearance potentials of various dissociative electron-impact ionization products. The results of that study indicated that we had as impurity species SF_4, Cl_2, and FCl. Furthermore, the sample used in Birmingham for swarm experiments was subjected to gas chromatographic mass spectrometry. No separation of gases occurred with the columns used. However, when the 70 eV impact ionization spectrum was recorded and compared with the published cracking pattern [14], it suggested that SF_4 was indeed an impurity. These impurities are taken into account when determining the anion products resulting from electron attachment to SF_5Cl. The presence of SF_4 and FCl as impurities is not surprising, given that these are the two molecules used in the synthesis of SF_5Cl. Fenzlaff et al. [6] synthesized their own sample, and mention that their only impurity was a small amount of SF_2O resulting from hydrolysis of SF_4. We may therefore expect hydrolysis impurities in our sample. An inspection of a 70 eV electron-impact mass spectrum recorded by us using the Innsbruck sample shows peaks at 83 amu (SFO_2^+), 86 amu (SF_2O^+) and 105 amu (SF_3O^+). Consistent with this observation, when looking at the negative anions produced with 0 eV electron attachment, we observe 83 amu (SFO_2^-) and 105 amu (SF_3O^-) peaks as impurity anions.

3. Results and discussion

3.1. Anion products

Electron attachment to SF_5Cl in the electron energy range 0–14 eV generates a large number of anionic products. The fragment ion SF_5^- is found to be the dominant species in the Innsbruck electron beam experiment as well as in the Kaiserslautern LPA/EXLPA and Rydberg electron transfer (RET) data. To illustrate this, Fig. 1a shows a high resolution mass scan of the anion products, obtained with the beam apparatus when the electron energy was set at approximately 0 eV. Fig. 1b presents an anion mass spectrum due to RET at high principal quantum number of potassium ($n \approx 140$), taken at somewhat lower mass resolution. Note that both spectra have a logarithmic intensity scale. There is good qualitative agreement between the two data sets although the relative intensities differ somewhat. The presence of F^- in Fig. 1a is a result of the lower electron energy resolution used in the beam studies (~0.3 eV) compared to that used in the laser photoelectron attachment experiments, i.e., the electron energy width associated with the 0 eV electron beam is sufficient to access the F^- channel. The SF_6^- anion present in the mass spectrum of Fig. 1b is a result of an SF_6 impurity. However, its intensity is so low that any contribution of electron attachment to SF_6 to form SF_5^- will be negligible. The very weak peak observed at about 70 amu (Cl_2^-(?)) in Fig. 1a must also be due to electron attachment to a small unknown impurity in the beam apparatus. The only effect the impurity could have on the anion yield curves will be associated with Cl^- (i.e., electron attachment to the impurity could be resulting in Cl_2^- and Cl^-). However, given the low intensity of the mass 70 peak, we may safely assume that any contribution to the Cl^- intensity will be negligible.

Table 1 summarizes results from the present and the earlier [6] electron beam studies, as well as those from the present

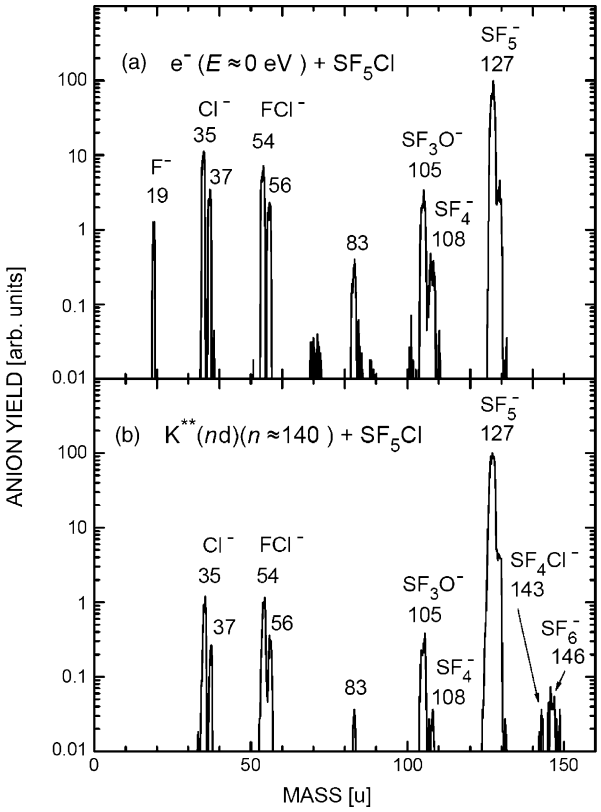

Fig. 1. Anion mass spectra due to near-zero energy electron attachment to SF_5Cl. (a) Free electron attachment ($E \approx 0$ eV; Innsbruck experiment). (b) Rydberg electron transfer involving highly excited $K^{**}(nd)$ atoms ($n \approx 140$) with the ion optics optimized for SF_5^- ions.

and from an unpublished RET study. The latter work involved $Ar^{**}(nd)$ Rydberg atoms ($n = 14$–30)[1,2] and the SF_5Cl gas sample also used by Fenzlaff et al. in [6]. The quoted intensity ratios for the Innsbruck experiment (normalized to 100 for the SF_5^- yield at near-zero electron energy) were obtained from the count rate at the highest peak of the respective anion yield curves, with allowances made for isotopes, electron current and sample gas pressure. The Innsbruck mass spectrometer was kept at the lowest possible resolution to minimize mass discrimination effects. There will be discrimination as a result of any kinetic energy that the product anions receive, and no allowance can be made for this without further information of the kinetic energy release following dissociative electron attachment. The production of the anions SF_5Cl^- and SF_5^- only occurs through the resonance at 0 eV. It can be seen from Table 1 that, with the exception of SF_5^-, there is relatively good agreement between the intensities obtained in the present set of studies and that of Fenzlaff et al. [6].

Before we present attachment spectra for eight of the product anions and compare with those of Fenzlaff et al. [6], we summarize the thermochemistry of the exothermic pathways for the

Table 1
Anion products observed, peak positions and relative intensities for electron attachment to SF_5Cl obtained from the electron beam study (Innsbruck), compared with other data

Anion	Peak position (eV)	Relative intensities			
		Innsbruck	Berlin[a]	K'lautern[b]	K'lautern[c]
SF_5Cl^-	0	0.003	(0.08)		
SF_5^-	0	100		(100)	(100)
	≈0.5		(2)		
SF_4^-	≈4.0	0.02			
SF_3^-	≈8.1	0.3			
SF_2^-	≈11.2	0.02			
FCl^-	0	8	4	3	1–5[d]
	≈8.5	0.2	0.4		
F_2^-	≈8.5	0.07	0.02		
Cl^-	0	14	(12)	5	1–5[d]
	≈8.5	1.3	3.3		
F^-	≈0.5	8.6	8		
	≈4.4	6.8	3.5		
	≈8.5	2.3	1.2		

[a] Electron beam data [6]; normalization for Cl^- anion (=12).
[b] RET ($Ar^{**}(nd)$, $n = 14$–30)[1,2].
[c] RET ($K^{**}(nd)$, $n = 140$); present work.
[d] Variations of intensities reflect changing detection efficiencies for different operation modes of mass spectrometer.

anion products at zero electron energy:

$$e^- + SF_5Cl \rightarrow SF_5Cl^-, \qquad \Delta H^\circ_{298} = -EA(SF_5Cl) \quad (2)$$

$$e^- + SF_5Cl \rightarrow SF_4Cl^- + F, \qquad \Delta H^\circ_{298} < -1.34\,eV \quad (3)$$

$$e^- + SF_5Cl \rightarrow SF_5^- + Cl, \qquad \Delta H^\circ_{298} = -1.26\,eV \quad (4)$$

$$e^- + SF_5Cl \rightarrow FCl^- + SF_4, \qquad \Delta H^\circ_{298} = -0.52\,eV \quad (5)$$

$$e^- + SF_5Cl \rightarrow Cl^- + SF_5, \qquad \Delta H^\circ_{298} = -1.08\,eV \quad (6)$$

To calculate the enthalpies for these reactions we have used $\Delta_f H^\circ_{298}(SF_5Cl) = -10.8$ eV [14], $\Delta_f H^\circ_{298}(SF_4Cl) = -7.9$ eV from a selected ion flow tube study by Atterbury et al. [15] and the electron affinities of SF_5 and SF_4Cl to be 3.80 eV [16] and ≥5.04 eV (unpublished work by us), respectively.

Thermodynamics indicates that the production of SF_4^-, SF_3^-, SF_2^-, SF^-, and F_2^- via dissociative attachment of 0 eV electrons to SF_5Cl is endothermic (and compatible with the spectra recorded at Berlin, see below):

$$e^- + SF_5Cl \rightarrow SF_4^- + FCl, \qquad \Delta H^\circ_{298} = 0.86\,eV \quad (7)$$

$$e^- + SF_5Cl \rightarrow SF_3^- + FCl + F, \qquad \Delta H^\circ_{298} = 2.87\,eV \quad (8)$$

$$e^- + SF_5Cl \rightarrow SF_2^- + FCl + F_2, \qquad \Delta H^\circ_{298} = 6.27\,eV \quad (9)$$

$$e^- + SF_5Cl \rightarrow SF^- + F_2 + FCl + F, \qquad \Delta H^\circ_{298} = 8.92\,eV \quad (10)$$

$$e^- + SF_5Cl \rightarrow F_2^- + SF_3 + Cl, \qquad \Delta H^\circ_{298} = 3.69\,eV \quad (11)$$

Although these anions cannot be produced by attachment of electrons with zero energy, we did observe zero energy peaks of low intensity for all these anions using the Innsbruck beam

[1] A. Fras, T. Kraft, E. Illenberger, M.-W. Ruf, H. Hotop, 1990, unpublished results.
[2] A. Fras, Diplomarbeit, Univ. Kaiserslautern, 1990, unpublished results.

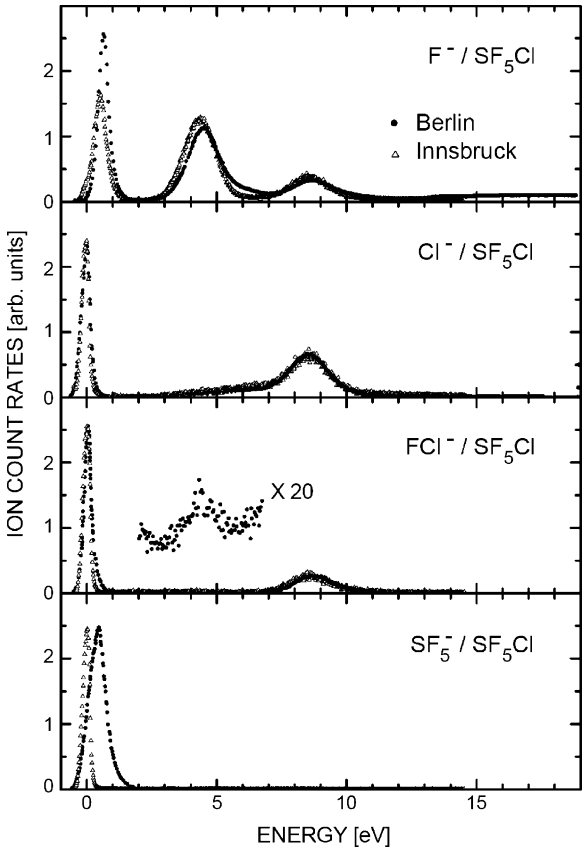

Fig. 2. Attachment spectra for F^-, Cl^-, FCl^-, and SF_5^-. Full circles: Berlin experiment, open triangles: Innsbruck experiment. For F^-, Cl^-, and FCl^- the anion yields of the two experiments were individually normalized to equal size at the higher energy resonance around 8.5 eV while for SF_5^- the low-energy peak was adjusted to the same height. In the Innsbruck spectra for Cl^- and FCl^-, the intensity of the measured near-zero energy peak was divided by factors of 3.5 and 6, respectively.

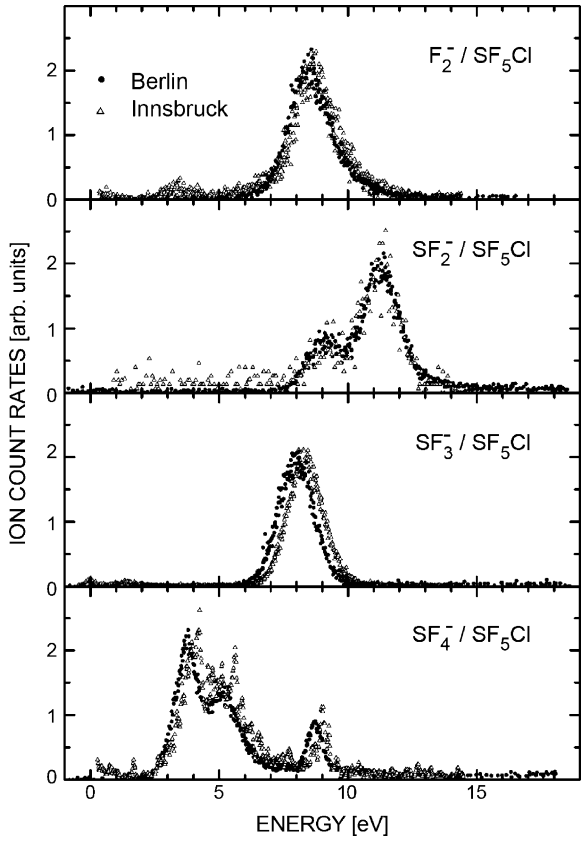

Fig. 3. Attachment spectra for F_2^-, SF_2^-, SF_3^-, and SF_4^-. Full circles: Berlin experiment, open triangles: Innsbruck experiment. The anion yields of the two experiments were normalized to equal size at a higher energy resonance individually for every anion (see text).

apparatus. Given the thermochemistry and the fact that Fenzlaff et al. [6] did not observe any zero energy peaks for these anions, we conclude that they must result from a secondary process, e.g., anion-molecule reactions in the beam. We note here that the direction of propagation of anions in the quadrupole mass spectrometer in the Innsbruck beam apparatus lies along that of the molecular beam. Alternatively, it has been suggested that such spurious low-energy peaks are a result of electron detachment from the parent anion in an accelerating region (a so-called "Trojan" electron), resulting in high energy electrons, which can attach to the molecules in the neutral beam [17]. Note that the anion mass spectra observed at near-zero electron energy at Kaiserslautern did not exhibit contributions due to the above anions.

In Fig. 2 we compare the energy-dependent attachment spectra for formation of the most intense anions F^-, Cl^-, FCl^-, and SF_5^- from SF_5Cl, as measured in Innsbruck, with those reported by Fenzlaff et al. [6] (subsequently denoted as Berlin data). The widths of the near-zero energy peaks are resolution limited, in both the Innsbruck and in the Berlin data. As can be inferred from the shape of the spectrum for the SF_5Cl^- parent anion (which consists of a resolution limited near-zero energy peak) the data in [6] were taken with an effective resolution (FWHM) of about 0.25 eV. The Innsbruck spectra were measured with an effective resolution of close to 0.30 eV, as concluded from a comparison of the width of the near-zero energy peaks for Cl^-, FCl^-, and SF_5^- formation with our highly resolved LPA/EXLPA spectra (see below). In Fig. 3 we show the spectra for those anions which only exhibit resonances at higher electron energies and have rather small cross sections. The spurious zero energy peaks have been removed from the Innsbruck data for clarity.

Good overall agreement in the respective spectral shapes and positions is observed for all the anions except for SF_5^-. With the intensity normalization used in Fig. 2, the signals of the near-zero energy peaks for Cl^- and FCl^-, however, differ substantially (see caption of Fig. 2). The shape of the SF_5^- spectrum due to Fenzlaff et al. [6] differs substantially from that obtained in Innsbruck: the maximum of the former is located at about 0.3 eV and the width is much broader than that of the Innsbruck spectrum which peaks at near-zero energy (as do the LPA/EXLPA spectra, see below). We note that the shape of the SF_5^- spectrum shown in [6] is similar to that for SF_5^- formation from SF_6 [11] at gas temperatures around 300 K. This could indicate that the gas sample which was present during the measurement of the SF_5^- spectrum shown in [6] contained a substantial fraction of SF_6.

The attachment spectrum for F^- formation shows three distinct bands peaking at about 0.5, 4.2, and 8.5 eV. Good agreement

is found between the respective shapes of the three bands measured in Innsbruck and Berlin, while the peak locations and the relative intensities of the bands differ somewhat. That the low-energy resonance for F^- production peaks above zero energy (at approximately 0.5 eV, see Fig. 2), confirms the observations of Fenzlaff et al. [6] and is consistent with the thermodynamics which predicts F^- formation to be endothermic by 0.30 eV (using the enthalpy in Eq. (3), the estimate 5.04 eV for the electron affinity of SF_4Cl quoted above, and the electron affinity for the F atom of 3.401 eV [18]; the same value is obtained when one combines the heats of formation for SF_5Cl and SF_4Cl (see above) and that for the F atom (+0.8 eV) with the electron affinity of F):

$$e^- + SF_5Cl \rightarrow F^- + SF_4Cl, \qquad \Delta H^\circ_{298} = 0.30\,\text{eV} \tag{12}$$

The set of branching ratios we obtained in the new beam experiments are also consistent with the thermal swarm measurements in Birmingham [7], for which SF_5^- (90%) was observed as the dominant species. The rather intense parent anion SF_5Cl^- (10%) is attributed to collisional stabilization by the carrier gas CO_2 in the high pressure environment of the swarm apparatus. The fact that we did not observe the minor dissociative electron attachment channels (i.e., Cl^- and FCl^-) could also be the result of carrier gas collisions with SF_5Cl^- formed in the initial attachment process (at 1 bar pressure, the time between collisions of any formed anion with the carrier gas particles is of the order of 100 ps). These collisions may remove a sufficient amount of internal energy so that the dissociation paths towards Cl^- and FCl^- are closed. We also note that anions with small intensities could escape detection as a result of insufficient sensitivity.

The only major difference between the earlier swarm measurements [7] and this present study corresponds to the observation that SF_4^- appeared to be the dominant anion in the non-thermal swarm measurements for mean electron energies above 0.2 eV [7]. Very recently we have repeated this measurement in Birmingham, and this observation is confirmed. However, it is difficult to reconcile this observation with the thermochemistry (reaction (7)), even in a swarm environment in which the electrons have a broad energy distribution. The explanation for the observation must lie with the now known presence of SF_4 impurity in the Birmingham SF_5Cl sample, and the higher cross section for electron attachment of low-energy electrons to SF_4 compared to that of SF_5Cl. We note that Fenzlaff et al. (see Fig. 7 in [6]) reported SF_4^- only at higher electron energies.

3.2. Highly resolved cross sections for the formation of Cl^-, FCl^-, and SF_5^- anions at low energies

In Kaiserslautern, highly resolved attachment spectra were measured at low energies with both the LPA and the EXLPA method for production of the dominant fragment anion SF_5^-; for the less abundant anions Cl^- and FCl^- results were only obtained with the EXLPA method. In Fig. 4 we show the absolute cross section for SF_5^- formation, as obtained from the combined LPA/EXLPA

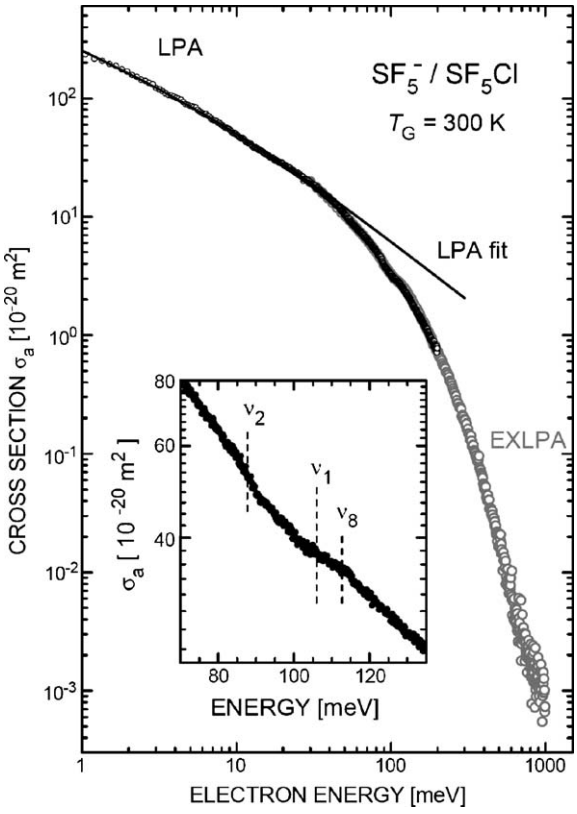

Fig. 4. Absolute cross section for SF_5^- formation from SF_5Cl (combined LPA/EXLPA data) measured over the range 0–1 eV.

anion yield with reference to the thermal rate coefficient $k_{th}(SF_5Cl) = 2.0 \pm 0.3 \times 10^{-8}\,cm^3\,molecule^{-1}\,s^{-1}$ of Mayhew et al. [7]. Here, we use the fact that SF_5^- is by far the dominant anion channel, the fraction of all the other anions formed at near-zero energies being no more than about 10% which is within the uncertainty (±15%) of the thermal rate coefficient.

At energies below 30 meV, the LPA cross section is well described by an analytical fit function of the form [10]:

$$\sigma_{LPA}(E) = (\sigma_0/E)[1 - \exp\{-\beta E^{1/2}\}] \tag{13}$$

with $\sigma_0 = 616 \times 10^{-20}\,m^2\,meV$ and $\beta = 0.53\,meV^{-1/2}$. The parameter β characterizes the energy range ($\beta^2 E > 0.1$) above which substantial deviations from the limiting s-wave attachment behaviour $\sigma_{LPA}(E \rightarrow 0) = \sigma_0 \beta E^{-1/2}$ occur [10].

Towards higher energies, the cross section drops rapidly by a factor of about 500 as the electron energy rises from 0.05 to 0.5 eV. In view of the fact that most of the excess energy – if deposited into translational energy of the fragments – will be carried away by the lighter neutral fragment Cl, we expect that the measured energy dependence of the anion yield is not significantly influenced by discrimination effects (i.e., reduced anion detection efficiency towards higher electron energy). Some structure is observed in the range 80–120 meV which may be due to coupling of the attachment channel with the vibrational excitation channels $v_2(A_1) = 1$, $v_1(A_1) = 1$, and $v_8(E) = 1$ with onsets at 87.7, 106.0, and 112.7 meV, respectively [19,20].

In Fig. 5, we compare the anion yields for Cl^- and FCl^- production, measured with the EXLPA method over the energy

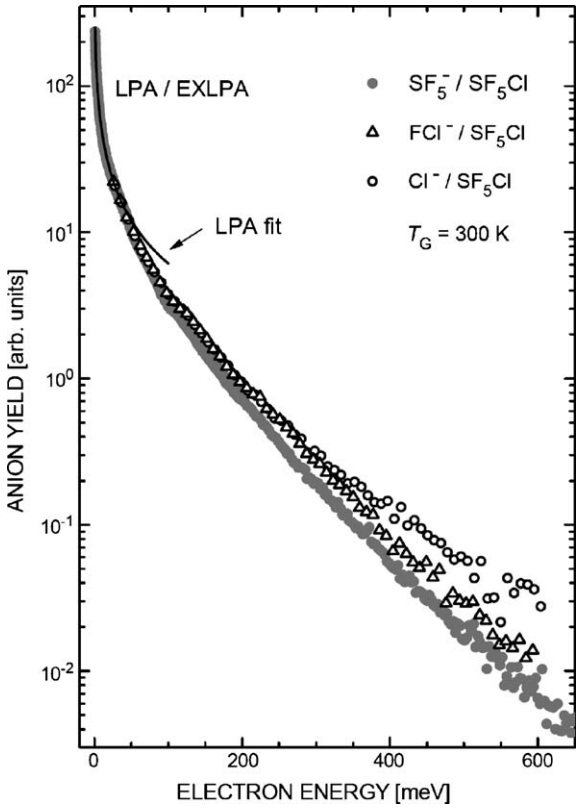

Fig. 5. Energy-dependent yields $Y(E)$ for the formation of Cl^- (open circles), FCl^- (open triangles), and SF_5^- anions (grey full circles) due to electron attachment to SF_5Cl molecules ($T_G = 300$ K) over the range $E = 1$–600 meV. To within ±20%, the ratio $Y(Cl^-)/Y(FCl^-)$ is constant at energies below 0.35 eV. The curve denoted LPA fit represents the energy dependence of the fit to the SF_5^- cross section (Eq. (13)).

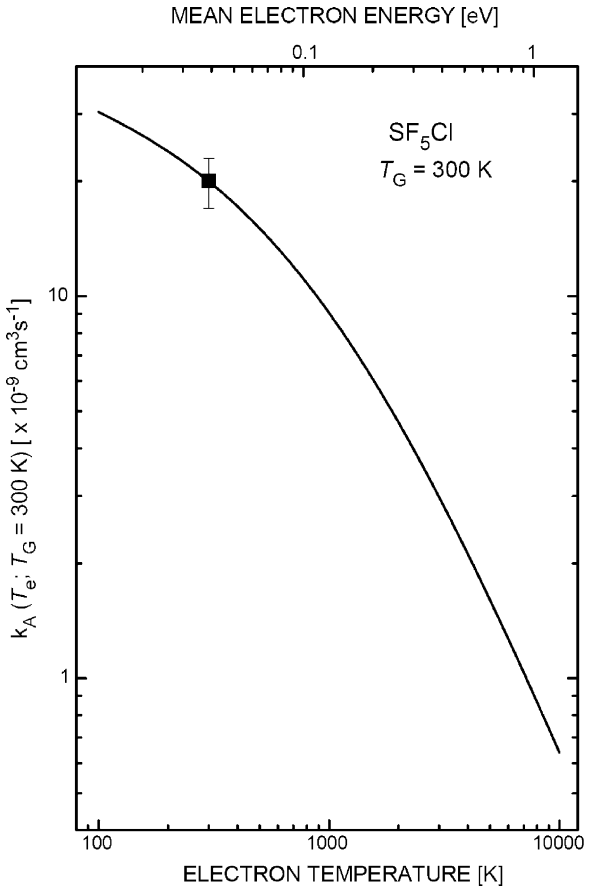

Fig. 6. Calculated dependence of thermal rate coefficient for electron attachment to SF_5Cl as a function of electron temperature for the fixed gas temperature $T_G = 300$ K. The filled square denotes the value of the thermal ($T_e = T_G = 300$ K) rate coefficient $2.0 \pm 0.3 \times 10^{-8}$ cm^3 $molecule^{-1}$ s^{-1} to which the LPA/EXLPA attachment cross section was normalized.

range 0.03–0.6 eV at a resolution of about 25 meV, with that for SF_5^- formation. For both Cl^- and FCl^-, the shape of the EXLPA anion yield at low energies is essentially the same as the one for SF_5^- formation, and it drops steeply with rising energy in a way similar to the observation made for SF_5^- production. Although LPA data were not taken for Cl^- and FCl^-, it can thus be assumed that the energy dependence of the yield for these two ions follows the LPA fit function (Eq. (13)) found to be a good description of the SF_5^- cross section at energies below about 40 meV (see Figs. 4 and 5). Viewed in more detail, the ratios $Y(Cl^-)/Y(SF_5^-)$ and $Y(FCl^-)/Y(SF_5^-)$ exhibit a slow, nearly linear increase by about 35% from 30 to 300 meV, followed by a similar rise for the ratio $Y(FCl^-)/Y(SF_5^-)$ up to 600 meV while the ratio $Y(Cl^-)/Y(SF_5^-)$ increases somewhat more strongly. These observations are in line with the trend that the lighter anions are somewhat favoured towards higher electron energies. This may be due to higher survival probabilities for the lighter anions on their way from the primary attachment zone to the dissociation region.

Since the shapes of the yield for the three major anions SF_5^-, Cl^-, and FCl^- are very similar (especially at low energies), the absolute cross section for SF_5^- formation (Fig. 4) can be used to calculate the dependence of the total electron attachment rate coefficient on electron temperature T_e at the fixed gas temperature $T_G = 300$ K (note that the cross section for SF_5^- formation was calibrated with reference to the total thermal electron rate coefficient at equal electron and gas temperature $T_e = T_G = 300$ K). We assume the electron ensemble to be Maxwellian (as given in connection with Eq. (1)) with a mean electron energy $\langle E \rangle = (3/2)k_B T_e$. The result of this calculation is shown in Fig. 6 for $T_e = 100$–10,000 K ($\langle E \rangle = 0.013$–1.3 eV). To our knowledge, no results from electron swarm experiments have been reported so far for comparison. As expected from the shape of the SF_5^- cross section, the rate coefficient decreases monotonically with rising mean electron energy.

4. Conclusions

Using mass spectrometric detection of the product ions, we have measured partial energy-dependent yields for eight anions due to electron attachment to SF_5Cl molecules. For the three anions Cl^-, FCl^-, and SF_5^-, which are observed at near-zero electron energy, we report highly resolved anions yields, as obtained with two variants of the laser photoelectron attachment (LPA) method. Thermal swarm measurements have been used to place the relative LPA cross sections on an absolute scale. Using these absolute attachment cross sections, we have calculated the energy-dependent attachment rate coefficients for

SF_5Cl molecules at the fixed gas temperature of 300 K for electron temperatures 100–10,000 K (mean electron energy range 0.013–1.3 eV).

In terms of energy positions, shapes and widths of the electron attachment resonant peaks, the Innsbruck data are in good agreement with the results of an earlier beam study of Fenzlaff et al. [6]. In addition, with the exception of the SF_5^- channel, there is rather good agreement between the relative intensities of these peaks. For SF_5^- formation, Fenzlaff et al. [6] observe a rather broad peak with a maximum at about 0.5 eV while the present results convincingly demonstrate an s-wave attachment process with a cross section rising towards zero energy and dominating anion formation from SF_5Cl at low electron energies.

Acknowledgments

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